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Lubrication

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THIS ISSUE

Application of
Radioactive Tracers in
the Petroleum Industry

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Application of Radioactive Tracers in the Petroleum Industry

THE basic phenomena of radioactivity which are the foundation of the use of radioactive isotopes as tracers have been known since the very early part of this century. However, it is only recently, as a result of the construction of large nuclear reactors made possible by the discovery of nuclear fission, that a wide variety of different radioactive isotopes has become available in great quantity. This availability of radioactive isotopes is one of the most important peace time results of the tremendous effort which was put forth during the war to obtain the knowledge required to manufacture and control the atomic bomb. Because there exists a wide selection of cheap radioactive isotopes, their application to a variety of tracer problems has been growing at an accelerated pace.

This article will present very briefly the background information required to understand those properties of radioactive isotopes which make them useful as tracers, and then will describe at some length a number of successful applications of radioactive tracers in the petroleum industry, with the main emphasis on lubrication problems.

RADIOACTIVITY

The chief facts which must be known about radioactivity in order to understand the use of radioactive materials as tracers are few and simple. Every chemical element possesses a number of isotopes, which are atoms having the same nuclear charge[1] and the same number of electrons circulating around the nucleus, but differing in the masses[1] of their nuclei. Some isotopes of the same element are stable and some are radioactive. The simplest example is hydrogen, with charge 1, which has three isotopes: ordinary hydrogen (hydrogen-1), deuterium (hydrogen-2) and tritium (hydrogen-3). Ordinary hydrogen and deuterium are stable, but tritium is radioactive, emitting an electron and transforming into the stable but rare isotope of helium with charge 2 and mass 3.

An important property of isotopes is that all isotopes of the same element behave chemically in essentially the same way. A specific isotope may be described by writing the element name followed by the mass number, e.g., cobalt-60.

The most important function of a radioactive atom is to emit energetic radiation. This radiation may include the emission of alpha particles (helium nuclei), beta particles (electrons), and gamma rays (electromagnetic radiation of short wavelength). Only those radioactive atoms which emit

[1]The unit of charge is the charge on the electron. The unit of mass is approximately the mass of one hydrogen atom.

TABLE I
Characteristic Data for Radioactive Isotopes Often Used as Tracers

Isotope	*Half-life*	*Beta Particle Energy Mev*	*Gamma Ray Energy Mev*
Hydrogen-3	12.5 years	0.018	None
Carbon-14	5700 years	0.155	None
Phosphorous-32	14.3 days	1.718	None
Sulfur-35	87.1 days	0.167	None
Iron-59	46.3 days	0.26; 0.46	1.1; 1.3
Cobalt-60	5.25 years	0.31	1.17; 1.33
Strontium-90	25 years	0.54	None
Antimony-124	60 days	0.6; 3.2	0.6; 1.7
Iodine-131	8.04 days	0.32; 0.6	0.08; 0.28; 0.36; 0.64

beta and/or gamma radiation are important for tracer work, because the alpha particles have too little penetrating power. Although the electrons or beta particles emitted by a radioactive atom are much less penetrating than are the gamma rays, even the weakest can be measured usefully. It is customary to express the energy of the radioactive radiation in units of million electron volts or Mev[2].

A second important property of a radioactive atom is its half-life. This is the time required for half of any given number of such atoms to decay, i.e., to undergo the radioactive transformation (emit the particular kind of radiation) which characterizes them. Half-lives vary from small fractions of a second to millions of years. For tracer purposes, a radioactive isotope is most useful when it has a half-life which is not much longer than the time required to perform whatever experiment is involved. For such an isotope the radioactivity initially present does not persist for a long time after the experiment is over, reducing any possible safety hazard.

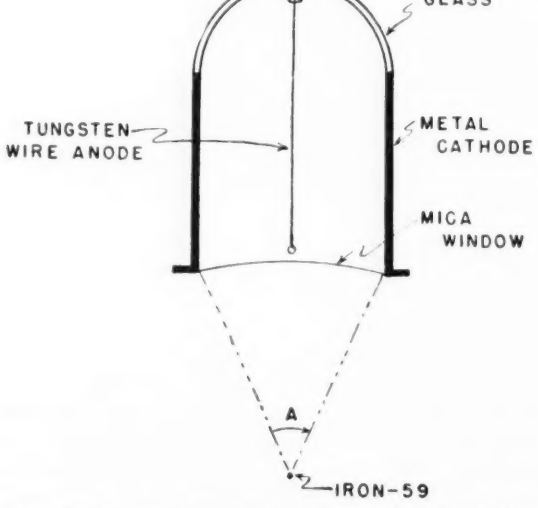

Figure 1 — Schematic cross-section of an end-window Geiger counter with a point sample. Only the radiation emitted in directions included in the cone of apex angle A will enter the counter.

The word tracer often implies trace quantities, and it is here that the radioactive tracer shines. The very high efficiency with which the radiation emitted can be detected makes possible the measurement of extremely small amounts of radioactive material. For example, as little as 10^{-16} gram of iodine-131, which has an 8.04 day half-life, can be detected easily.

Table I gives some characteristic data for several radioactive isotopes which often are used as radioactive tracers. It is important to remember that both the kinds of radiation emitted and the energies of the radiation are uniquely characteristic of the isotope. For example, iron-59 is the only isotope which emits beta particles with energies of 0.26 and 0.46 Mev and simultaneously gamma rays with energies of 1.1 and 1.3 Mev. The combination of kind and energy of radiation with the half-life makes identification completely unambiguous.

MEASUREMENT OF RADIOACTIVITY

In the measurement of radioactivity the important quantity is the activity or the number of radioactive disintegrations per second. The detecting device produces an output of "counts" per second which is proportional to the activity. The activity of a sample containing a given radoactive isotope is given by the following relationship

$$\text{activity in disintegrations/second} = \frac{0.693\ (\text{number of radioactive atoms present})}{\text{half-life in seconds}}$$

Activity usually is expressed in curies, one curie

[2]One Mev is the amount of energy which any particle having unit charge will acquire in falling through a voltage difference of one million volts. One Mev is equivalent to 1.6×10^{-6} erg.

being equal to 3.7×10^{10} disintegrations per second. Obviously for any element there will be a definite number of atoms (and hence mass of material) which correspond to one curie, but this number will vary from element to element.

Every kind of radiation emitted by radioactive nuclei has the distinctive and important property of producing *ionization*. This means that when the beta particles or gamma rays emitted by the nucleus pass through any material, whether it be gas, liquid or solid, orbital electrons are ejected from the atoms of the material, leaving each ionized atom positively charged. Both the positively-charged atom and the electron ejected from it are called ions, and the two together are referred to as an ion pair.

A single beta particle from a radioactive nucleus will produce several hundred ion pairs per centimeter of its path in air. A gamma ray produces only about one ion pair per cm in air.

The extreme sensitivity which is possible in detecting radioactivity results from the development of instruments which can detect the presence of a small number of ion pairs, even down to a single ion pair. One such device, called a Geiger-Mueller counter, is shown schematically in Figure 1. It usually consists of a hollow metal cylinder which has a thin tungsten wire stretched along its axis and which forms part of an enclosure filled with gas at a low pressure. A voltage in the neighborhood of 1000 volts applied between the wire and the cylinder almost, but not quite, causes an electric discharge in the gas. If ionizing radiation passes through the gas and produces at least one ion pair, a momentary electric discharge does occur. The occurrence of this discharge means that the single ion pair has triggered off a phenomenon which produces about 100,000,000 more ion pairs. The effect of this much larger number is used to produce a pulse in an associated electric circuit which causes it to register one count. If more than one ion pair is produced by the beta particle or gamma ray, the group is formed so closely together in time that only one magnified discharge occurs. Provided that the number of beta particles or gamma rays which enter the counter per second is not too large (less than 5000 per second) the counter will discharge and record a count for each group of one or more ion pairs.

The gas pressure in the usual Geiger counter is such that any beta particle which traverses it is sure to produce at least one ion pair and trigger the counter. This is not true of gamma rays. Many of them will travel the length of a counter without producing a single ion pair. The usual counter detects only about one per cent of the gamma rays passing through it.

An idea of the sensitivity of detection of radioactive materials can be obtained from the following

Figure 2 — A Geiger counter set up to measure the phosphorus-32 activity in samples of oil.

considerations. Suppose a Geiger counter is located near a sample containing iron-59 so that it will register or count 25 per cent of all the beta particles emitted. Suppose that the observed counting rate is 10 counts per second, so that the number of disintegrations per second in the sample is 40. Since the half-life in seconds (from Table I) is $46.3 \times 86400 = 4 \times 10^6$, the number of iron-59 atoms in the sample is $40 \times 4 \times 10^6 / 0.693 = 2.31 \times 10^8$ from the above activity relationship. This number of iron-59 atoms weighs only about 2×10^{-14} gram or one fiftieth of a millionth of a millionth of a gram.

Figure 2 shows an actual Geiger counter in a counting arrangement for measuring phosphorous-32 in oil. The counter is held by a rack which accepts a shelf at five different levels. The shelf, in turn, has a depression in which one can insert a dish of oil containing the phosphorous-32 one wishes to measure. The shelf and rack arrangement insure that the same fraction of the radiation emitted reaches the counter for each sample of oil. The disk to the right of the counter is a National Bureau of Standards sample of radium D and radium E of known activity. It is used to obtain a day-to-day standardization of the counter. This counting arrangement is shown in use in Figure 3. The samples being measured were quite radioactive so the shelf is down to the third position below the

Figure 3 — The Geiger counter set-up connected to a scaling circuit which allows one to determine counts per unit time.

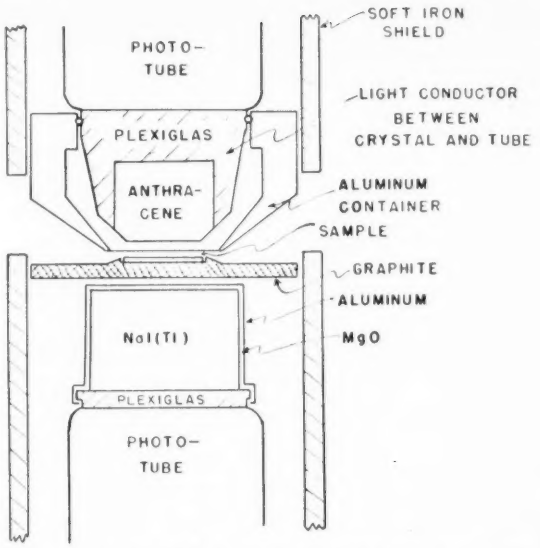

Figure 4 — A counting arrangement using two scintillation counters, one sensitive to beta particles and the other sensitive to gamma rays.

counter and no lead shield is being used around the counting arrangement. If the counting level is low, one must shield the counter to reduce the background from cosmic rays and radioactivity in the surroundings.

Another device for detecting ionizing radiation is the scintillation counter. Figure 4 shows two scintillation counters arranged to measure beta and gamma radiation at the same time[3]. In principle, a scintillation counter is nothing more than a phototube watching a substance which gives a flash of light when ionizing radiation strikes it. Anthracene crystals have been found to be sensitive to beta particles, while thalium-activated sodium iodide crystals are the material of choice for gamma scintillators. The fact that the scintillator, or flash light producer, is much denser than the rarefied gas used in a Geiger-Mueller counter greatly increases the probability of ion-pair production by gamma rays.

In the arrangement shown in Figure 4, each time there is a light flash in the anthracene, the phototube translates this into an electrical pulse which is registered by a counting circuit. Light flashes from the sodium iodide crystal are registered in a second circuit. As a further refinement, each time flashes occur simultaneously in both crystals, a third register is activated. In this way one can tell which gamma rays and which beta particles occur at the same time.

There are two interesting differences between these two radiation detectors. The first is that the Geiger-Mueller counter delivers the same size sig-

[3]D. Maeder and P. Staehelin, Helv. phys. Acta *28*, 193-226 (1955), "The complex beta transformation of sodium-25 and aluminum-25."

nal to its associated electrical circuit no matter how many ion pairs were produced in the initial traversal of the gas filling, while the scintillator delivers a light flash which is proportional in intensity to the number of ion pairs produced. The second difference is that after breakdown a Geiger-Mueller counter requires time to be restored to counting condition while, as soon as the light flash has died out, the scintillator is ready to detect another event. This means that a scintillation counter can be used to measure the energy of radiation since the number of ion pairs produced is proportional to the energy delivered to the scintillator by the radiation.

There are other devices, such as ionization chambers, proportional counters, and electroscopes, which also detect radiation by means of the ionization produced. Photographic film, on the other hand, detects radiation in much the same way that it detects light. A latent image is produced which can be developed in the same way as an ordinary photograph. Film is often employed to locate the position of radioactive materials. When a piece of film is held against a sample, those areas which are opposite radioactive parts will be blackened. This way of detecting radioactivity is called autoradiography.

WAYS OF USING RADIOACTIVE TRACERS

There are four simple ways in which radioactive isotopes can be used as tracers. The first and simplest is to fasten a piece of radioactive material to any object which is to be traced. For example, a small container of cobalt-60 bolted to a pipeline scraper has been used to keep track of the scraper[4] as it travels down the pipeline, even though the pipe is buried to a depth of several feet. A second example is the impregnation of the surface of a small quantity of cracking catalyst with a chemical containing cobalt-60 so that distribution and mixing of this tagged catalyst can be observed or traced when it is added to a full scale fluid catalyst cracking unit[5].

The second way involves mechanical similarity. For example, beads made from a radioactive ceramic to have the same diameter and density as standard cracking catalyst beads are used to measure the flow rate of the latter in a full scale cracking unit[6].

The third way makes use of solubility. Pipeline flow has been measured[7,8,9] by use of an oil-soluble compound (triphenyl stibnite) containing a radioactive isotope such as antimony-124, which emits a penetrating gamma ray. Figure 5 shows in a schematic way how this can be used. A Geiger counter located just before a valving system allows the operator in the pump house sufficient warning of the arrival of the radioactive interface so that he can open the valve to the storage tank and close the valve to the outgoing line. The arrival of a second radioactive interface at the end of that particular shipment would then warn him via the Geiger counter to reverse the valves. Claims are made that

[4] D. B. Scott, Nucleonics 9, No. 3, 68-7 (September, 1951), "Detection of scrapers in pipelines."

[5] A. J. Kinsella, Jr. and J. J. Mitchell, "A Study of Catalyst Mixing and Loss in Commercial Fluid Catalytic Cracking Units by Means of Radioactive Tracers." Presented at the Washington Meeting of the Atomic Industrial Forum, Inc. on Sept. 27, 1955.

[6] D. E. Hull and R. R. Bowles, Oil and Gas Journal *51*, No. 46, 295-9 (March 23, 1953), "New use for radioactive tracers. Measuring catalyst flow rates in cat crackers."

[7] D. E. Hull and B. A. Fries, Oil & Gas Journal *52*, No. 9, 66-8 (July 6, 1953), "How radioactive control is applied — to a products pipeline."

[8] D. E. Hull and J. W. Kent, Ind. Eng. Chem. *44*, 2745-50 (1952), "Radioactive tracers to mark interfaces and measure intermixing in pipelines."

[9] D. E. Hull, J. W. Kent, and R. D. Lee, World Oil *129*, 187-8 (May, 1949), "Radioactivity in pipeline flow studies."

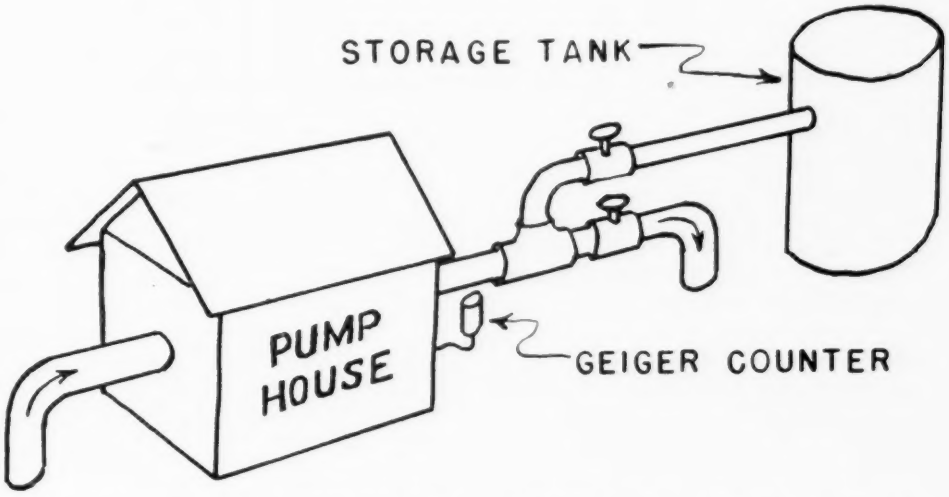

Figure 5 — A much simplified sketch of a pipe-line pumping station equipped with a Geiger counter to detect a radioactive interface marker.

such a system results in a saving of a considerable number of barrels of product which do not have to be rejected to a slop tank.

The fourth way uses chemical identity. An example is the use of carbon-14 to study the reaction of CO with iron to form iron percarbide[10]. A carefully reduced iron catalyst was partially carbided with CO containing some $C^{14}O$, so that some radioactive iron percarbide was formed. Carbiding was then continued with ordinary CO and it was found that the CO_2 produced by the reaction

$$2Fe + CO \longrightarrow Fe_2C + CO_2$$

contained some carbon-14. This result – that carbiding with ordinary CO over a partially carbided layer obtained with radioactive CO transfers radioactive carbon to the CO_2 produced – led to the development of a clearer picture of the details of the carbiding process.

RADIOACTIVE PISTON RING WEAR TESTS

Now that the meaning of radioactivity, the idea of a tracer, and methods of measuring radiation have been discussed, it is time to apply this knowledge to a lubrication problem. Reduction of ring wear in automotive engines is one of the functions of a lubricant. It has been measured in various ways: by weighing the rings before and after use, by measuring the reduction in length of special marks stamped into the rings, and by determining the increase in iron content of crankcase oil by chemical means. This last method, of course, works only if the rings are the sole iron parts of the engine which are wearing. But suppose one of the rings was radioactive. Then the radioactivity which would appear in the crankcase oil would be due entirely to wear from that ring. When S. W. Ferris[11] first had this idea, it was necessary to make the ring radioactive by first making special cast iron with a radioactive element incorporated in it and then machining out a piston ring. Today, things are much easier. An ordinary, commercial ring can be sent either to Oak Ridge National Laboratory or to the Brookhaven National Laboratory where it will be exposed to the intense slow-neutron fluxes of the nuclear reactors located at those places. Slow neutrons and ordinary iron react to give radioactive iron-59. For instance, if an iron piston ring was exposed to the typical Oak Ridge reactor neutron flux of 5×10^{11} neutrons per cm^2 per sec. for 30 days, it would have an iron-59 activity of 3300 disintegrations per sec. per milligram. It was assumed at the start of this article that a count rate of 10 cps, which corresponds to an activity of 36 disintegrations per second, was a convenient minimum count rate to detect. This would be the count rate from 1.1×10^{-5} gram of irradiated piston ring, which is a far cry from the 2×10^{-14} gram of pure iron-59 which would give the same count rate. However, it is still correct to call a method which will measure accurately 11 micrograms of iron a very sensitive method.

Almost as soon as the possibility existed of obtaining adequately radioactive piston rings representing commercial manufacture, wear tests were undertaken by their use[12]. A radioactive top ring was installed on the piston of a standard single-cylinder, 4¼-inch bore, four-cycle diesel engine. The engine was run for a short while to break in the ring. Then various oils were compared in the following manner. The engine and crankcase were carefully flushed. Then a charge of test oil was introduced. A sample of the oil was taken and its apparent radioactivity measured. This served as a blank. Such a blank is necessary because cosmic rays and, if the test is made near the engine, radioactivity in the surroundings will make the Geiger counter give a reading. The engine was run under the desired test conditions. Samples of oil were taken from the crankcase periodically to be assayed for radioactivity. These samples were returned immediately to the crankcase to keep the oil quantity constant.

The first question one could ask is: "Does the measured radioactivity actually give an accurate value for ring wear?" Careful calibration gave excellent material balances in this work. At the end of 12 hours, radioactivity indicated 24.6 mg. of iron worn from the ring. Its actual weight loss was 25.0 mg. At 55 hours, the corresponding values were 37.2 and 38.0 mg.

Even if this careful calibration is not carried out, one can still obtain accurate relative wear rates by running a standard oil under standard conditions between runs on test oils. An idea of the accuracy of this procedure is given by the fact that the average wear rate of 1.02 mg. per hr., determined from six standard runs interspersed among 18 tests, was found to have a standard deviation of only 0.03 mg. per hr. The usefulness of relative wear rate measurements is shown in Figure 6. These points were all determined in one day's operation. They demonstrated conclusively that wear rate increases with fuel sulfur content. While this, of course, is already well known from other work, the precision of the results and the rapidity with which they were determined is impressive.

[10]John J. Mitchell, J. Chem. Phys. *21*, 1153-9 (1953), "A study of the formation of iron percarbide."

[11]S. W. Ferris, U. S. Patent 2,315,845, (April 6, 1943), assigned to The Atlantic Refining Company, "Wear Test method and composition."

[12]P. L. Pinotti, D. E. Hull, and E. J. McLaughlin, SAE Journal 57, 52-4 (June, 1949), "Harness nuclear fission to measure engine wear," and SAE Quarterly Transactions 3, No. 4, 634-8 (October, 1949), "Application of radioactive tracers to improvement of fuels, lubricants, and engines."

One of the main advantages of the piston ring wear method of studying engine lubrication is that the engine need not be taken apart after each run. This means that engine conditions can be kept constant and that one is not plagued with trying to interpret variable break-in wear. However, running tests in engines under such carefully controlled and reproducible conditions might not give results which would carry over to actual operation of automotive engines in the field. Two groups have carried out tests which do confirm the validity of the carry-over. In one case [13], it was shown that radioactive rings used in Cooperative Oil Test engines and used as top front rings in ordinary passenger cars gave the same relative rating to two experimental oils. In the other case[14], the comparison was made between the effect of oils on piston ring wear as measured by the radioactive ring method under FL-2 conditions and an average cylinder wear in a fleet of taxicabs.

Radioactive piston ring wear tests have been used in Great Britain[15] and in Russia[16] for determination of lubricating oil properties. The Russians were particularly concerned about the correspondence between various methods of measuring wear. They made several series of runs in which chemical analysis of the crankcase oil, measurement of change in length of marks on the ring, change in weight of the ring, and radioactivity in the crankcase oil were all used to determine wear. They found that all these methods agreed within experimental error. The Russians also broke up an irradiated piston ring and measured the radioactivity of various parts to make sure that the ring was uniformly radioactive. If the outer surface of the ring had been more radioactive than the interior, calibration would have shifted during a wear rate run.

As each laboratory became satisfied that the method was accurate as well as far less time consuming than conventional methods, a large amount of lubricant testing was carried out. One laboratory using a Coordinating Fuels Research (CFR) engine and a Cooperative Oil Test (COT) engine has developed[17] an impressive series of results. In the COT engine they varied the upper cylinder wall temperature with the results shown in Table II, which clearly demonstrate how an additive can reduce low-temperature wear. Other engine variables which they investigated were air-to-fuel ratio at low temperatures, incipient knocking, oil viscosity, and the amount of sulfur or of alcohol in the fuel.

One very interesting effect at 65°F. jacket temperature was that, when a change was made from a non-additive oil to a low wear oil, over 5 hrs. of running were necessary before the new low wear rate was established. The change was almost instantaneous when the oil was changed back to a non-additive oil. This suggests that, after a high wear situation, something very much like break-in must occur. The ring has to wear in again just as if it had been been a newly installed ring.

From reading the reports of successful radioactive ring-wear tests one concludes that the main advantages of the method are (1) the sensitivity for detection of incipient wear, (2) the reduced

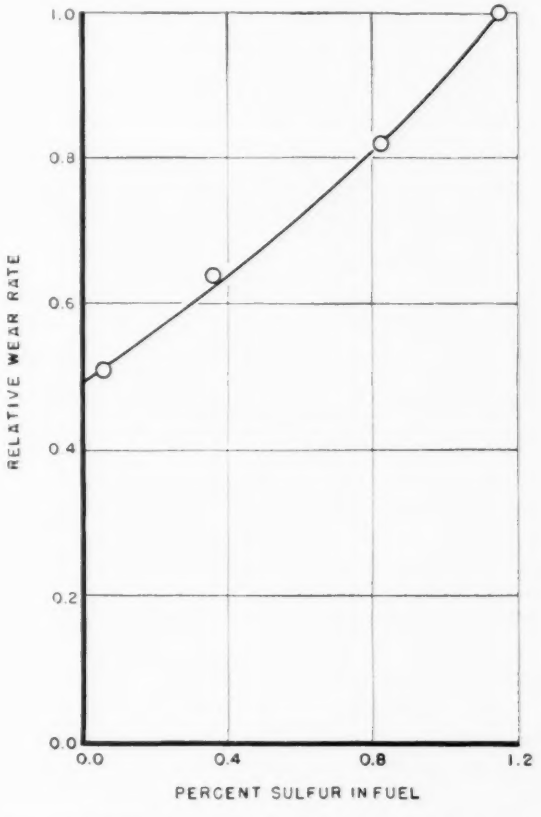

Figure 6 — Dependence found by Pinotti, Hull, and McLaughlin between piston ring wear and fuel sulfur content in a single-cylinder, 4-cycle, 4¼-inch bore diesel engine operated at 1400 rpm, 150°F. oil sump temperature, 800°F. exhaust temperature, and 175°F. jacket temperature.

[13] H. R. Jackson, SAE Transactions *61*, 233-6 (1953), "Laboratory and field wear tests using radioactive tracers."

[14] F. W. Kavanagh, SAE Transactions *61*, 231-2 and 236 (1953), "Engine wear — comparison of radioactive and field measurements."

[15] Chemical and Engineering News *31*, 4086-8 (1953), "Piston Ring treated in atomic pile determines engine wear rapidly"; A. Dyson and K. R. Williams, J. Inst. Petroleum *39*, 524-30 (1953), "The use of radioactive-tracer technique in the wear-testing of engine lubricating oils."

[16] Y. S. Zaslavskii, G. I. Shor, and F. B. Lebedeva, Izvest. Akad. Nauk SSSR, Otdel. Tekh. Nauk, No. 1, 54-60 (1954). Translation: RJ-232, Associated Technical Services, P. O. Box 271, East Orange, New Jersey. "Accuracy of engine wear investigations by the radioactive tracer methods."

[17] H. R. Jackson, F. C. Burk, L. J. Test, and A. T. Cowell, SAE Quarterly Transactions *6*, 518-30 (July, 1952), "Some phenomena of engine wear as revealed by radioactive tracer technique."

TABLE II
Top Ring Wear in COT Engine

	Jacket Temperature			
	180°F.	*120°F.*	*100°F.*	*80°F.*
Non-additive oil	0.1 mg/hr	0.8 mg/hr	2.4 mg/hr	—
Additive oil	0.1 mg/hr	0.4 mg/hr	—	0.5 mg/hr

time required for a wear test, (3) the fact that a test oil and a standard oil can be compared under exactly the same engine conditions, and (4) the opportunity for making a continuous record of wear which allows detection and measurement of transient effects.

One could ask if there are times when the radioactive ringwear method would be unsuccessful. There are. If the iron particles worn off the ring do not stay suspended in the crankcase oil, the method just will not work. A tantalizing situation of this sort occurs when the operating conditions cause formation of sludge which builds up in the engine, breaks loose to circulate with the oil, and then is held up again for a period. In some tests this sludge appears to act as a scavenger for iron particles. The apparent result, in terms of radioactivity of the crankcase oil, will then be, first, a very low wear rate, second, sudden onset of high wear, and, finally, negative wear. Since this last is impossible, it is a sign that the method is being applied to a situation where it will not work.

Radioactive piston rings can be used in a slightly different way to obtain additional useful information. Metal transfer from ring to cylinder wall has been determined by use of rings plated with radioactive chromium[18]. After the engine was run under the desired conditions with the plated ring in place, the engine was dismantled, the cylinder surface cleaned with solvent, and a photographic film fitted into the cylinder. By use of a careful indexing procedure, the darkening of the film gave the location of chromium transferred to the cylinder wall in terms both of the position of the ring on the piston and also of the position of the piston in the cylinder. Thus, a ring which no longer moved in its groove gave rise to an obvious lack of radioactivity opposite the opening between the ends of the ring. As might have been expected, more material was transferred to the cylinder wall at the top of the piston travel. One could carry out this same sort of work with irradiated ordinary cast iron rings.

Safety Considerations

Before leaving the subject of radioactive rings, it would be well to consider the possible danger from a radioactive ring. Earlier in this article a typical radioactivity was given at 3300 disintegrations per second per milligram of piston ring. Since a ring weighs about 15 grams, a whole ring will have an activity of about 5×10^7 disintegrations per second. At a distance of one foot, this ring would deliver[19] a dose of gamma radiation of about 20 milliroentgens (or "mr") per hour. The roentgen is a unit of radiation dose. Suffice it to say that the maximum permissible dose for people is 300 mr per week[20]. A man should not work for more than 15 hours per week at a distance of one foot from such an unshielded ring. Fortunately, the dose drops off as the inverse square of the distance so that at 4 ft., the ring would furnish a dose rate of only about 1¼ mr per hr. which is quite safe. Also, heavy metal barriers cut radiation efficiently. An iron shield, 0.9 in. thick, will reduce the radiation dose from the piston ring by a factor of two.

RADIOACTIVE GEAR WEAR TESTS

What has just been said about piston rings is even more important for gears. A gear can very easily weigh 1 lb. This would raise the radiation level by a factor of 30. One should spend a maximum of one-half hour at one foot from such an unshielded gear in any one week. Figure 7 shows the installation in test equipment of such a gear at Southwest Research Institute. One man is holding the 560-gram gear with long-handled tongs which keep him more than 1 ft. away from the gear. His partner is measuring the radiation level. It is his responsibility to be sure that no one approaches the gear close enough to exceed an agreed-on maximum level. Both men are wearing rectangular badges. These contain film which registers the amount of radiation received by each man. The person installing the gear not only must be a skilled mechanic but also must be calm, cool, and collected. A dropped radioactive gear is a dangerous object and has to be dealt with promptly and correctly.

[18] J. T. Burwell and S. F. Murray, Nucleonics 6, No. 1, 34-7 (January 1950), "Radiochromium plating for friction studies."

[19] In this calculation it was assumed that the ring is a point source which emits just one-half the radiation that the same activity of radioactive cobalt would emit. The value of 14.5 roentgens per hour for 1 curie at 1 ft. was taken from P. M. Frazier, C. R. Buchanan, and G. W. Morgan, Isotopics 5, No. 1, 9-29 (January 1955), "Radiation safety in industrial radiography with radioisotopes."

[20] National Bureau of Standards Handbook 59, "Permissible doses from external sources of ionizing radiation," Sept. 24, 1954.

The equipment in which the gear is being installed is a Ryder, four-square, power-circulating gear machine[21]. The amount of iron worn off the test spur gear is being studied in terms of the load necessary to give scuffing and the E. P. characteristics of the lubricant.

Similar studies are in progress at other laboratories[22]. At the Engineering Institute of the University of Michigan, a four-square machine is being used to test a radioactive sun gear run against planet gears[23]. The results of one set of runs illustrate one of the difficulties which can be experienced. First, a sun gear was run with an SAE 30 mineral oil until the gear was badly worn. Then an extreme-pressure type lubricant was substituted to see what it could do for a "worn-out" gear. While the wear rate was substantially reduced, pieces of the gear flaked off because of metal fatigue caused during the early part of the run. These pieces circulated in the oil and gave erratic radioactivity readings. It was still possible, however, to obtain an average wear rate so the test was not completely lost.

Autoradiographs were made of the teeth of the planet gear after several of the runs. SAE 30 mineral oil gave rise to a large amount of metal transfer from the sun gear to the planet gear. EP gear oil, on the other hand, gave rise to very little metal transfer.

BASIC LUBRICATION PHENOMENA

Although wear studies on actual parts are important in development of lubricants and can be made on components other than rings and gears, as, for instance, on cutting tools[24] for study of cutting oil performance, they do not aid directly in learning what is the true nature of lubrication. The use of chemical tracers is more suited for this type of work. In one example, an additive was made by sulfurizing[25] mixed olefins with radioactive sulfur. Since the olefins were derived from petroleum wax, this additive was one actually used in lubrication practice and found to have beneficial properties. When various bearing materials were immersed at 88°C. (190°F.) in oil containing this radioactive additive, a radioactive film was formed on the metal surfaces. This film was not soluble in benzene or carbon disulfide so it certainly was not a simple oil film. On many bearing materials it was invisible to the eye; on others it was apparent as an opalescence. Plots of radioactivity of the metal surface against time of immersion showed that the metal acquired a maximum coating after 40 hours. Further immersion did not increase the radioactive film.

The film forming tendencies of tridecanoic acid[26] and of amyl iodide[27] have also been studied by the use of radioactive tracers incorporated in the film forming material. The opposite tack was taken in a study[28] in which the metal was made radioactive. Strips of gold, platinum, zinc, cadmium, and copper were made radioactive by exposure to a slow neutron flux. They were then carefully extracted with benzene and finally exposed to benzene solutions of octadecyl alcohol, stearic acid, and ethyl stearate. The solutions were then assayed for

[21] A. Hundere, C. G. Lawrason, and J. P. O'Meara, paper presented at ASLE Annual Meeting, Chicago, April 13-15, 1955, "Neutrons, gamma rays, and wear."

[22] Chemical and Engineering News *30*, 776 (1952), "'Hot' gears for lube oil research."

[23] F. L. Schwartz and R. H. Eaton, paper presented at SAE National Tractor Meeting, Milwaukee, Sept. 13-16, 1954, "Wear rates of gears by the radioactive method."

[24] M. E. Merchant and E. J. Krabacher, J. Appl. Phys. *22*, 1507-8 (1951), "Radioactive tracers for rapid measurement of cutting tool life"; M. E. Merchant, H. Ernst, and E. J. Krabacher, paper presented to the ASME Semi-Annual Meeting, Cincinnati, June 15-19, 1952, "Radioactive cutting tools for rapid tool testing."

[25] G. L. Clark, S. G. Gallo, and B. H. Lincoln, J. Appl. Phys. *14*, 428-34 (1943), "Radiosulfur tracer study of sulfurized lubrication addition agents."

[26] A. Gemant, J. Phys. Colloid Chem. *54*, 569-76 (1950), "Radioactive tracer study of an aliphatic acid in hydrocarbon oil"; J. Electrochem. Soc. *99*, 279-84 (1952), "Film formation on metals in hydrocarbons."

[27] E. Rabinowicz, Nature *170*, 1029-30 (1952), "Autoradiography of metal surfaces using a radiochemical method."

[28] F. P. Bowden and A. C. Moore, Research *2*, 585-6 (1949); Trans. Faraday Soc. *47*, 900-8 (1951), "Physical and Chemical adsorption of long chain compounds on metals."

(*Courtesy of Southwest Research Institute*)

Figure 7 — Installing a radioactive gear in the Ryder four-square gear testing machine at Southwest Research Institute.

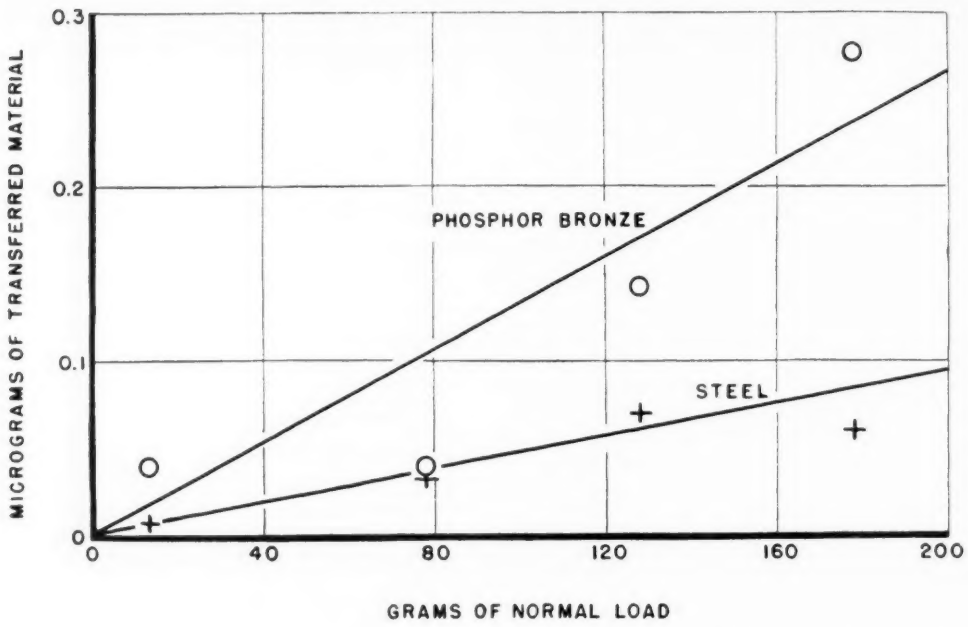

Figure 8 — The transfer of material from a copper-beryllium flat to hemispherical bronze and steel riders as a function of the load on the rider.

radioactivity. The alcohol solutions showed no radioactivity. The stearic acid solutions in contact with gold and platinum showed no radioactivity, but those in contact with the other metals very definitely did. Ethyl stearate solutions showed only slight radioactivity for the same metals. Since fatty acids, above their own melting points, lubricate zinc, cadmium, and copper, but not gold and platinum, the radioactive results are taken to indicate that a soap is formed between the fatty acid and the zinc, cadmium, or copper; that the soap is maintained in a layer adjacent to the metal surface; and that the soap is the actual lubricant.

One can go a step behind the films which might be formed during lubrication and study friction, the property lubrication combats. One of the basic methods of making such studies has been to drag a slider over a flat. Considerable new information has been derived from this method by making the slider radioactive[29,30] by making the flat radioactive[31], or by making the wear fragments radioactive[32] after the sliding process was completed.

In a typical experiment[31] a $\frac{3}{8}$-in. diameter hemispherical rider rubbing on a radioactive copper-beryllium flat was used. The amount of material transferred from the flat to the rider was determined by measuring the radioactivity acquired by the rider. The inherent high sensitivity of the method was such that 10^{-4} microgram of transferred metal could be detected.

The polished flat, with a surface roughness of 2.5 to 3.0 micro-inches, was exposed to the deuteron beam of the M.I.T. cyclotron to induce radioactivity. The flat was then electropolished to remove any possibility of loose radioactive material being present on the surface. The rider was pushed over the flat at a velocity between 3 and 4 mm/sec. Figure 8 shows that more material is transferred at higher loads, which was expected. It also shows more material was transferred to the bronze, which was softer than the copper-beryllium flat, than to the steel which was harder than the flat. This was not expected. Parenthetically, it might be mentioned that Figure 8 also shows considerable scatter in the data. This led to subsequent tests being replicated five to eight times.

The difference between steel and bronze is made more understandable by studying material transferred as a function of the roughness of the rider. Bronze riders (Brinell hardness, 190 kg/mm^2) with surface roughness of 2.5-3.0 micro-inches picked up 0.019 $\pm$ 0.002 microgram, whereas those with roughness 9.0-13.0 micro-inches picked up 0.014 $\pm$ 0.002 microgram. The smoother rider

[29] E. Rabinowicz and D. Tabor, Proc. Roy. Soc. (London) *208A*, 455-75 (1951), "Metallic transfer between sliding metals: an autoradiographic study."

[30] E. Rabinowicz, J. Appl. Phys. *24*, 367 (1953), "On the looseness of wear fragments."

[31] B. Sakmann, J. T. Burwell, and J. W. Irvine, Jr., J. Appl. Phys. *15*, 459-73 (1944), "Measurement of the adhesion component in friction by means of radioactive indicators."

[32] E. Rabinowicz, Proc. Phys. Soc. (London) *64A*, 939-40 (1951), "A study of metal transfer during sliding, using radioactivation analysis."

picked up slightly more material. On the other hand, the steel riders (Brinell hardness, 640 kg/mm²) showed a marked change in material transferred M (in micrograms) with surface roughness R (in micro-inches). A straight line, $M = 0.0020 + 0.0024R$, gave a reasonably good fit to the data from 1 to 7 micro-inches roughness. Thus, the rougher the steel rider, the more material it picked up. One can argue that the harder rider plows through the flat (Brinell hardness 310 kg/mm²) and tears off pieces which adhere to the rider. The amount torn off the flat depends on the number and size of the asperities on the rider. The softer rider shows the reverse trend with more material transferred to the smoother surface.

When it was found that soft steel riders behaved much as did the bronze riders, a series of riders of different hardness but with the same smoothness was tested. The results obeyed fairly well the relation $M = 20/B$ over a range of Brinell hardness, B, from 190 to 640 kg/mm².

The influence of lubricant on friction was found[29] to be smaller than on metal transfer. A well-lubricated surface showed friction reduced by a factor of 20 but metal transfer reduced by a factor of 20,000 over the same surface unlubricated. In fact, two lubricants which gave essentially the same coefficient of friction were found to give amounts of metallic transfer differing by a factor of 20. A poor lubricant showed transfer approximately proportional to load, the behavior shown in Figure 8 for unlubricated surfaces. However, a good boundary lubricant, although showing much reduced transfer, gave an increase in transfer with load which was greater than linear.

It was also found that the well-known change in lubricant properties with temperature near the melting point of the lubricants tested, such as palmitic acid and copper palmitate, was also accompanied by an abrupt change in amount of metallic transfer. In addition it was found with these lubricants that, at temperatures 25 to 100°F. higher, the lubricant behavior deteriorated to that of a "poor" lubricant.

SELECTED RESEARCH APPLICATIONS

There are two radioactive isotopes which naturally comes to mind for research with petroleum products, namely, carbon-14 and tritium, or hydrogen-3.

Until recently tritium has found little use because its beta radiation has so little penetrating power that it cannot be detected with ordinary counters[33]. However, methods of overcoming this difficulty by employing a liquid scintillation counter have been devised, and the use of tritium in tracer studies is increasing rapidly. On the other hand, carbon-14 has been used in many and varied research problems.

A use of carbon-14 somewhat different from the usual mechanism studies was a measurement of the rate of exchange of CO between the chemisorbed phase on iron and the gaseous phase in contact with it[34]. In this work radioactive CO was chemi-

[33] A very interesting non-tracer use of tritium was reported by Leon Dorfmann and F. J. Shipko of General Electric (Chem. & Eng. News 33, 1653 (1953)). They mixed tritium with acetylene and measured the amount of chemical reaction caused by the tritium B particles. The main products were benzene and cuprene. The tritium did not react chemically with any of the other compounds in the mixture.

[34] R. P. Eischens, J. Chem. Phys. 19, 377 (1951), J. Am. Chem. Soc. 74, 6167 (1952), "Isotopic exchange rates as criteria of surface heterogeneity."

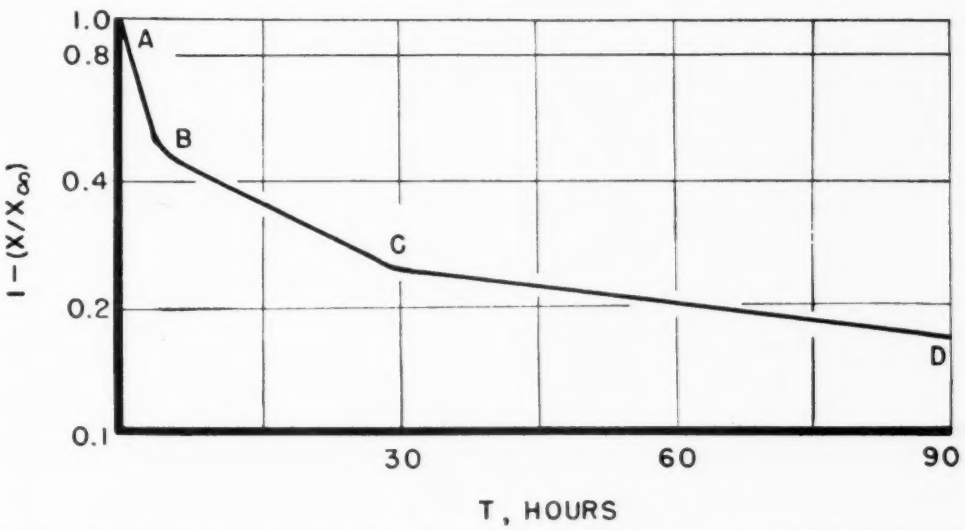

Figure 9 — A semilogarithmic plot against time of the fraction of the equilibrium concentration of radioactivity which has not yet exchanged. Here X is the concentration of radioactivity which has built up in the gas phase at time T after ordinary CO has been put in contact with radioactive CO chemisorbed on iron.

sorbed on carefully reduced iron. Then the gas phase was pumped away, and ordinary CO put in its place. The appearance of radioactivity in the gas phase was measured as a function of the time from the introduction of ordinary CO. In ordinary exchange reactions if x is the concentration of radioactivity in the gas phase after equilibrium has been reached, then the concentration x at time t is given by $\ln [1 - (x/x_\infty)] = - Rt(a+b)/ab$, where R is the rate of exchange and a and b are the fractions of the total gas which are, respectively, chemisorbed and in the gas phase. Plotted on a semi-logarithmic scale, this relation would give a straight line. When the actual data were plotted, as in Figure 9, a curve with several straight line portions, A-B, B-C, and C-D, was found. This same situation arises in biological experiments, and the equations have been completely worked out[35] which allow this curve to be interpreted as the result of the same number of simultaneous exchange rates as there are straight line portions.

This can be taken, in the case of CO chemisorbed on iron, to indicate that there are, in turn, the same number of chemisorbed phases. Thus, the iron surface must not be homogeneous. On the other hand, it is not completely heterogeneous. The exchange curve shown in Figure 9 indicates that there are only three ways in which CO is chemisorbed. Thus there are only three kinds of iron surface.

These examples are only two chosen from a large number of chemical tracer studies which are of direct interest to the petroleum industry. Of the common elements, only oxygen and nitrogen have no convenient radioactive counterpart, so possibilities for chemical tracer work are practically unlimited.

ANALYTICAL POSSIBILITIES

Besides the actual radioactive tracer work on the effect of lubricants on wear and on the phenomena basic to lubrication, there have been uses of radioactivity, not directly connected with lubrication, which are suggestive of such application. One of these has to do with the absorption of radiation in matter. Since the amount of radiation absorbed depends both on the radiation and also on the material it traverses, it was only natural to suggest[36] that this dependence would furnish a means for analysis. Practical analytical apparatuses giving accurate, rapid analyses for sulfur[37] in otherwise reasonably pure hydrocarbons and for hydrogen[38] in hydrocarbons have been built and tested. The first of these simply measures the absorption of the radiation from iron-55 in the sample; the second measures the absorption of strontium-90-yttrium-90 radiation in the sample. Proper calibration with known materials relates these absorptions to sulfur content in the first case and to hydrogen content in the second. To obtain hydrogen percentage, one must also determine the density of the sample. Such a hydrogen determination takes 5 minutes and has a precision of 0.02 weight per cent hydrogen.

Another analytical method, called "activation analysis", is based on the same process as that used in making piston rings radioactive. Neither carbon nor hydrogen are very susceptible to being made radioactive by neutrons, but the usual metallic impurities in oil are. One measures the induced radioactivity to determine the amount of metal present. Vanadium in crude oil[39] was one successful determination made by this method. The outstanding characteristic of the method is its sensitivity. As little as 10^{-3} microgram of many of the elements[40] can be measured.

While only activation analysis has been used[32] in lubrication research, both methods offer either very rapid or very sensitive procedures which would be useful in specific problems.

CONCLUSIONS

Just as in so many other fields of endeavor, the easy availability of radioactivity has made possible research on lubrication that would otherwise be difficult or impossible. The various wear studies using radioactive parts are ample justification for this statement. But, in addition, the use of radioactive tracers to study additive action and friction phenomena yields basic information which will allow improvement of lubricants.

Not all of the possible uses of radioactivity in lubrication research have been exploited. This article has listed properties of radioactivity in a general way and described uses of radioactivity in allied fields with the hope that further applications to lubrication problems will become apparent to the reader.

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[36] G. Herzog, U. S. Patents 2,534,352 (Dec. 19, 1950) and 2,613,325 and 2,613,326 (Oct. 7, 1952), assigned to The Texas Company, "Methods of determining proportions in compositions of substances."

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